A Potential Mechanism for the Abiotic Production of Ammonia

Matthew C. F. Wander
Department of Geosciences
SUNY at Stony Brook
Stony Brook NY, 11790
UNITED STATES
mwander@notes.cc.sunysb.edu

James D. Kubicki, PhD.
Dept. of Geosciences
The Pennsylvania State University
UNITED STATES

Martin A. A. Schoonen, PhD.
Department of Geosciences
SUNY at Stony Brook
UNITED STATES

Ammonia is one of the essential reactants in prebiotic synthesis of C-H-O-N compounds, such as amino acids. While virtually all ammonia today is produced either biologically via nitrogen fixation, or industrially via the Haber-Bosch process, on a prebiotic Earth it must have been produced abiotically. The reaction of ferrous Iron absorbed onto Goethite reducing dinitrogen gas to ammonia is thermodynamically favorable:

$$6Fe^{2+}_{(ads)} + N_{2(aq)} + 12H_2O_{(l)} \rightarrow 6\alpha\text{-}FeOOH_{(goethite)} + 2NH_{3(aq)} + 12H^{+}_{(aq)}$$

At alkaline pH, the reaction is spontaneous, utilizing the low hydronium concentration to enhance the redox stability. Therefore this reaction is a candidate for ammonia production in the Hadean Ocean.

More important than spontaneity is the issue of mechanism and rates which is the focus of this study. The reaction proceeds through two "stable" intermediates: N_2H_2 (diimid) and the second is N_2H_4 (hydrazine). Diimid is produced through two sequential Proton Coupled Electron Transfer (PCET) reactions: the first inner sphere, to prevent radical production, and the second either inner or outer sphere to reduce the intermediate $Fe^{4+}_{(aq)}$. Diimid disproportionates upon production to hydrazine and dinitrogen gas via a double hydrogen atom transfer. Ammonia is produced from hydrazine via two sequential PCET reactions equivalent to Diimid's production.

This work utilizes high level Density Functional Theory calculations, combined with Marcus theory to estimate rates for the reaction's essential steps. These rates will then be compared with subsequent experimental studies of both light and dark reactions.